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Applicant(s): DOW GLOBAL TECHNOLOGIES INC.

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TRACTION FLUID COMPOSITION

The present invention relates to a novel traction fluid compound, a process for its preparation, a traction fluid composition incorporating the novel traction fluid compound, and a process for use of these compositions in traction drive mechanisms.

A traction drive fluid is a fluid used in friction driving mechanisms employing rolling contact, such as an automobile or industrial continuously variable transmission and a hydraulic machine. A traction fluid to be effective needs to have high traction coefficient and to be stable against heat and oxidation and also to be inexpensive.

Various types of compounds have been described in the literature and used commercially as traction mechanism fluids, alone or in combination with a base stock hydrocarbon fluid.

K. H. Hentschel, the influence of molecular structure on functional behavior of lubricating fluids. 2: low coefficient of traction", J. Synth. Lubr. (1958), 2(3), 239-253, discloses the usefulness of various polyesters as traction fluids. Polymers of ethylene oxide (EO), propylene oxide (PO), EO/PO triblock, random EO/PO tetrahydrofuran terpolymer, random EO/PO tetrahydrofuran quaterpolyether, random EO/PO 3,3-dimethyloxepan quaterether, and random EO/PO 1,2-epoxydecane tetrahydrofuran quaterether have been evaluated.

U.S. Patent No. 4,525,290 (Tsubouchi et al) discloses the use of 1,1-di(tetrahydronaphthyl)alkane having from 2 to 4 carbon atoms, 1,1-di(bicyclohexyl)alkane having from 2 to 3 carbon atoms, and 1-tetrahydronaphthyl-1-cyclohexylethane as drive traction compounds exhibiting reduced change of traction coefficient over a wide range of temperature.

U.S. Patent No. 5,259,978 (Yoshimura et al) a traction fluid comprising (a) a diester compound derived from cyclohexanol and dicarboxylic acid or derived from a diol and cyclohexane carboxylic acid, and (b) branched poly-α-olefin.

U.S. patent No. 3,723,320 (Herber et al) discloses the use of cyclohexane epoxide as an acid scavenger and corrosion inhibitor in an aircraft hydraulic fluid.

U.S. Patent No. 3,925,217 (Green et al) discloses a compound having improved elastohydrodynamic film thickness in rolling contact bearing lubrication and bearing fatigue life. The compound comprises at least one cyclohexyl compound having two or more cyclohexyl rings, the rings being fused, concatenated, or linked by one or more C_1 to C_{16} alkylene, carboxy, or ether linkages, the compound having from 10 to 70 carbon atoms.

U.S. Patent No. 3,957,668 (Sheratte) and references cited therein disclose functional fluids used, for example, as lubricants, power transmission fluids and hydraulic fluids. These functional fluids comprise an epoxide compound such as 3,4-epoxycyclomethyl 3,4-epoxycyclohexane carboxylate in addition to a base stock fluid and a phosphate ester such as polymethacrylate and polyacrylate. In particular, U.S. Patent No. 3,957,668 (Sheratte) discloses a class of novel epoxy compounds which are polyesters of 4,5-epoxy-1,2-cyclohexane dicarboxylic acid for use as acid scavengers in functional or hydraulic fluids containing phosphonus ester and as viscosity index improvers.

U.S. Patent No. 4,076,642 (Herber et al) discloses a new class of monoepoxyethylenecyclohexyl compounds useful as acid scavengers and corrosion inhibitors in functional fluids.

European Patent Application No. 1 046 669 A1 (Renault) discloses the use of copolymers of ethylene oxide and propylene oxide having MW from 300 to 1200 as well as an alternative fluid based on neopolyol fatty acid esters useful as automobile fluids.

European Patent Application No. 0 943 599 A1 (Clariant GmbH) and its equivalent U.S. Patent No. 6,395,689 B1 disclose the use of terpene esters useful as traction fluids, solvents and intermediates. Traction coefficients as reported in Table 2 for diethylene glycol diisobornyl ether, triethylene glycol diisobornyl ether, dipropylene glycol diisobornyl ether, and tripropylene glycol diisobornyl ether are 0.090, 0.068, 0.099 and 0.086, respectively.

European Patent Application No. 0 082 967 (Optimol Oelwerke GmbH) discloses the use of bicycloheptane compounds with a cyclohexane ring bridged by a methylene group, where the ring system is substituted by one or more of cycloalkyl,

cyckloalkanoyl, cycloalkylcarbonyloxy, cycloalkoxycarbonyl and oxycycloalkyl wherein cycloalkyl groups can be further substituted with various groups. Traction coefficient for these compounds of up to 0.11 are reported in Figures 1 to 4.

Known traction fluids have disadvantages in that the traction coefficient decreases as temperature increases and their viscosity is too high at low temperatures. Also, they are generally difficult to manufacture and have high manufacturing costs associated with their production (cost up to U.S. $ 640 per gallon to produce). Their high cost to manufacture limits their commercial application. It has now been discovered new traction compounds that overcome the disadvantages of the known traction fluids. The new traction compounds exhibit high traction coefficient and are less costly to produce than known traction fluids. It has also been discovered that these new traction compounds not only exhibit high traction coefficients themselves but they also cause increase in traction coefficient of base stock traction compositions when blended therewith.

In one aspect the present invention concerns a traction compound having the following formulae

$$AB_n \qquad (I)$$

wherein A is a residue of a compound having from 1 to 10 active hydrogen atoms, B is a residue of a cycloalkene oxide having from 4 to 12 carbon atoms, or a cycloaliphatic epoxide having from 4 to 12 carbon atoms, and n is 1 to 10, with the proviso that n can be less than the number of active hydrogen atoms in compound A.

In another aspect, the present invention concerns a traction fluid composition comprising

(a) a traction compound of formula I described hereinbefore,

(b) a low viscosity base stock traction fluid, or any mixture thereof, and, optionally,

(c) a traction fluid additive such as, for example, an antioxidant, a corrosion inhibitor, a copper deactivator, an anti-wear additive, an extreme pressure additive, anti-foam additive, a viscosity modifier, and a dye.

In another aspect, the present invention concerns a process for the preparation of a traction compound of formula I described hereinbefore which process comprises reacting a cycloalkene oxide having from 4 to 12 carbon atoms, or a cycloaliphatic epoxide having from 4 to 12 carbon atoms with a compound having from 1 to 10 active hydrogen atoms in the presence of a polymerization catalyst.

The traction compounds of the present invention represented by Formula I above, hereinafter referred to as "traction polyglycols" or "traction polyglycol", are suitably prepared by the reaction cycloalkylene oxide with an active hydrogen-containing organic compound.

Non-limiting examples of cycloalkylene oxides having from 4 to 12 carbon atoms useful for the preparation of the traction polyglycols of the present invention are cyclobutene oxide, cyclopentene oxide, cyclohexene oxide, cycloheptene oxide, cyclooctene oxide, cyclododecene oxide, and 1,2,5,6-diepoxycyclooctane.

Non-limiting examples of cycloaliphatic epoxides having from 4 to 10 carbon atoms useful for the preparation of the traction polyglycols of the present invention are 1-(epoxyethyl) cyclobutane), 1-(epoxyethyl) cyclohexane, 1-(2,3-epoxypropyl)cyclohexane, and 1-(3,4-epoxybutyl)cyclohexane.

Representative of a compound having n number of active hydrogen atoms useful for the preparation of the traction polyglycols of the present invention are water, primary, secondary and tertiary aliphatic alcohols having from 1 to 10 carbon atoms, cycloalkyl alcohols having from 4 to 10 carbon atoms, glycols and polyols. Non-limiting examples of such compounds having n number of active hydrogen atoms are methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, cyclopropyl methanol, cyclobutanol, cyclobutane methanol, cyclopentanol, cyclopenten methanol, cyclohexanol, cyclohexyl methanol, cycloheptanol, cycloheptene methanol, cyclooctanol, cyclooctene methanol, cyclodecanol, ethylene glycol, propylene glycol, 1,4-butanediol, 2,3-butanediol, 1,2-pentane diol, 1,4-pentanediol, 1,5-pentanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol,

tetrapropylene glycol, dibutylene glycol, tributylene glycol, tetrabutylene glycol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), 2,3-dimethyl-2,3-butanediol (pinacol), Bisphenol A, 1,2- and 1,3-cyclopentenediol, 1,4-cyclohexenediol, 1,2- and 1,5-cyclooctenediol, cyclohexane dimethanol, glycerin, trimethylolpropane, pentaerythritol and sorbitol.

The reaction of the cycloalkylene oxide and the compound having n number of active hydrogen atoms is conducted at polymerization reaction conditions in the presence of a suitable known polymerization catalyst such as alkali or alkali earth metal hydroxide such as NaOH, KOH or $Ca(OH)_2$, boron trifluoride diethyl etherate, H_2SO_4, $SnCl_4$, alkyl alumino phosphonate, tri(pentafluorophenyl)borane, tri(pentafluorophenyl)aluminum, trimethylaluminum, phosphine oxide, phosphazenium, triflic acid, clay, alkyllithium and phospozene or $MgSiF_6$-$6H_2O$, and double metal cyanide. The polymerization reaction is conducted in an inert gas atmosphere such as under nitrogen and under conditions of temperature and pressure that are readily determined by a person of an ordinary skill in the art without undue experimentation. In general, the reaction is conducted at atmospheric pressure and the temperature is kept below 80 °C by a suitable means such as an ice bath since the polymerization reaction is an exothermic reaction.

The analysis of traction polyglycols of the present invention by known chromatographic techniques such as gas chromatography (GC) coupled with mass spectroscopy (MS) shows a range of oligomers containing from 1 to 4 cycloalkene oxide units. The average number of units is 2.

Traction polyglycols of the present invention are blended with base stock traction fluids for use as traction fluid compositions. The traction polyglycols are used in a traction effective amount. As used herein, the traction effective amount is an amount of the traction polyglycol that provides the base stock traction fluid with the desired traction property. The traction effective amount will vary depending on the traction polyglycol and base stock traction fluid employed. The traction effective amount of the traction polyglycol can be easily determined by a person of an ordinary skill in the art without undue experimentation. Typically, the traction effective amount is between 1 to 99, preferably from 15 to 45, most preferably from 20, to 40, weight percent based on the total weight of the traction fluid composition.

Any known base stock traction fluid that has low viscosity is suitable for use in the traction fluid composition of the present invention. Non-limiting examples of base stock fluid useful in the present invention are mineral oils, hydrotreated mineral oils, polyalphaolefins, phosphate esters, naphthenic oils, monobasic esters, dibasic esters, 1-8 carbon alkyl phthalates, polyol esters, dicyclopentadiene, dihydrodicyclopentadiene, dicyclohexylmethylpentane, and commercially available traction fluids such as, for example, fluids from Idemitsu Kosan Co, Ltd, or the Santotrac fluids available from the Findett Company, St Louis MO. Any mixture of these known base stock traction fluids is also suitable for use in the present invention. The base stock traction fluid should comprise at least 1, preferably at least 50, most preferably at least 70, percent by weight of the traction fluid composition of the present invention.

The traction fluid compositions of the present invention exhibit high traction coefficients due to the incorporation of the traction polyglycols of the present invention and are useful in various applications but are particularly useful for belt-continuously variable transmissions and torodial-continuously variable transmissions.

Various additives, conventionally used in traction fluids may also be added to the traction fluid composition of the present invention depending upon their application. Non-limiting examples of such additives are antioxidants, corrosion inhibitors, copper deactivators, anti-wear additives, extreme pressure additives, anti-foam additives, viscosity modifiers and dyes. Each of these additives is used in an amount typical for use of such additive in traction fluids. These amounts will vary with the additive used and a person of an ordinary skill in the art would know which additive and what amount of the additive to use depending on the application for which the traction fluid composition of the present invention is used.

The traction fluid compositions of the present invention exhibit high traction coefficients due to the incorporation therein of the polyglycols of the present invention. The polyglycols of the present invention also cause an increase of the traction coefficient of the base stock traction fluid when blended therewith.

The traction coefficient of a fluid is defined as the frictional force of a fluid in elastohydrodynamic conditions divided by the normal force of the contacting surfaces.

All parts, percentages and ratios herein are by weight unless otherwise indicated.

The invention will be further clarified by a consideration of the following examples which are intended to be purely exemplary of the present invention.

Example 1: Preparation of Traction Polyglycol A

Cyclohexanol (100.07 g) was mixed with cyclohexene oxide (195.96 g) in a 1 L, 5 neck round bottom flask fitted with a stirrer, nitrogen purge and heating and cooling control. Boron trifluoride diethyl etherate (BF_3 etherate) was added in 0.1 cc increments keeping the temperature below 70°C. Total BF_3 etherate added was 2.0 cc. Water (5 cc) was added to quench the reaction. The mixture (444.20 g) was transferred to a 1 L round bottom flask and placed on a rotary evaporator. The water and volatile species (29.48 g) were removed with heat (100°C) and vacuum (30 in Hg). A clear, viscous, pale yellow oil was obtained. The obtained product has the percentOH of 3.94 for a calculated hydroxyl equivalent weight of 431.5. This indicates that an average of almost two cyclohexene oxide units is present in the traction polyglycol chain.

Example 2: Preparation of Traction Polyglycol B

Cyclohexanol (199.79 g) was mixed with cyclohexene oxide (400.24 g) in a 1 L, 5 neck round bottom flask fitted with a stirrer, nitrogen purge and heating and cooling control. Boron trifluoride diethyl etherate (3.5 cc) was added in 0.1 cc increments keeping the temperature below 70°C. Water (10 cc) was added to quench the reaction. The mixture (602.99 g) was transferred to a 1 L round bottom flask and placed on a rotary evaporator. Water and volatile species (76.42g) were removed with heat (100°C) and vacuum (30 in Hg). A clear, viscous pale yellow oil with an average of 2 cyclohexene oxide units was obtained.

Example 3: Preparation of Traction Polyglycol C

Trimethylolpropane (49.59 g) was mixed with cyclohexene oxide (110.39 g) and heated to 50°C to dissolve trimethylolpropane. Additional cyclohexene oxide (111.12 g) and boron trifluoride (1.3 cc) was added over time keeping the temperature below 60°C. The reaction was quenched with 5 cc of water. Volatiles (50.39 g) were removed from the mixture (252.18 g) at 100°C and 30 in Hg vacuum for 1 hour after the end of gas evolution. A clear, viscous straw colored oil was obtained.

Example 4: Preparation of Traction Polyglycol

Trimethylolpropane (50.28 g) was mixed with cyclohexene oxide (113.85 g) and heated to 50°C to dissolve trimethylolpropane. The mixture was catalyzed with boron trifluoride (1.5 cc) keeping the temperature below 60°C. The reaction was quenched with 10 cc of water. Volatile species (9.81 g) were removed from the mixture (151.18 g) at 100°C and 30 in Hg vacuum for 1 hour after the end of gas evolution. A clear, viscous oil was obtained.

Example 5: Preparation of Traction Polyglycol E

2,3-Butanediol (98.88g) was mixed with cyclohexene oxide (216.59 g). The mixture was catalyzed with boron trifluoride in increments of 0.05 cc to 0.1 cc keeping the temperature below 60°C. Additional cyclohexene oxide (217.82 g) and catalyst (4.5 cc total) were added to the reaction mixture. The reaction was quenched with 15 cc of water. Volatile species (85.37 g) were removed from the mixture at 100°C and 30 in Hg vacuum for 1 hour after the end of gas evolution. . A clear, viscous straw colored oil was obtained.

Example 6: Preparation of Traction Polyglycol F

Trimethylolpropane (50.52 g) was mixed with cyclohexene oxide (113.13 g) and heated to 65°C to dissolve trimethylolpropane. Additional cyclohexene oxide (106.22 g) and boron trifluoride (1.1 cc) was added over time keeping the temperature below 60°C. The reaction was quenched with 5 cc of water. Volatile species (62.41 g) were removed from the mixture (262.97 g) at 100°C and 30 in Hg vacuum for 1 hour after the end of gas evolution. A clear, viscous yellow colored oil was obtained.

Example 7: Preparation of Traction Polyglycol G

Cyclohexane dimethanol (144.21g, 1 mole) and cyclohexene oxide (392.58g, 4 mole) were mixed in a 1 liter flask fitted with mechanical stirring, internal thermometer, nitrogen purge and reflux condenser. The mixture was cooled to 15°C. Boron trifluoride diethyl etherate (2.5 ml) was added in 0.2 incremental steps over a 1 hour period keeping the temperature below 60 °C by indirect cooling. After that the mixture was kept at 60 °C for two hours with heat. The catalyst was quenched with 5 ml of water. The volatile components and water were removed from the mixture at 100 °C and 20 in Hg vacuum for one hour. 515.22 g of the final product was obtained. This calculates to a loss of 4.16 percent of cyclohexene oxide. This resulting product, a viscous liquid, was characterized by molecular weight distribution through GC/MS:

Example 8: Traction Polyglycol H

Monoethyleneglycol (31.09 g) and cyclohexene oxide (197.37 g) were added to a 1 L flask equipped with mechanical stirring, ice bath, nitrogen purge and septum. The mixture was stirred and cooled to 10 °C. Boron trifluoride etherate (1.0 cc) was added in 0.2 cc increments over one hour period keeping the temperature below 80°C. The mixture was kept at 50 °C for one hour with heat. The reaction was quenched with 2 cc of water and the mixture (222.28) transferred to a 500 mL round bottom flask. Water and volatile components were removed from the mixture at 100°C and 30 in Hg vacuum for 1 hour after the end of gas evolution. The traction polyglycol obtained is a clear glassy solid at room temperature.

Example 9: Preparation of Traction Polyglycol I

The reaction was performed in a 1-liter automatic computer controlled autoclave marketed by Mettler company (special steel) equipped with a stirrer, a nitrogen purge and heating and cooling control. KOH (0.8212 g) was dissolved in water (18.02g) and charged in the reactor with cyclohexene oxide (392.58g). After nitrogen purge the reaction mixture were stirred at 600 rpm at 5.5 bar to nitrogen pressure and heated up to 220 °C. The pressure was raised up to about 18 bar with advanced temperature. The mixture was kept at 220 °C for six hours. During this time the pressure regressed to about 10 bar. After that the reaction mixture was cooled to 60 °C and transferred to a 1

L round bottom flask and placed on a rotary evaporator. 406.49 g of the final product were obtained. This calculates to a loss of 1.2 percent of cyclohexene oxide. This resulting product, a clear viscous fluid, was characterized by molecular weight distribution through GC/MS:

Examples 10 -13: Preparation of Traction Fluid Composition

Traction fluid compositions listed below were prepared according to the following general method: Blends of the traction polyglycols and base stock traction fluids were prepared in the laboratory in graduated glass beakers. Normally, the base stock traction fluid was weighed into the beaker followed by the traction polyglycol in an amount to provide the desired final weight percent active. The mixture was heated and stirred to effect complete solution of the traction polyglycol in the base fluid. The order of addition of the traction glycol and base stock traction fluid is not important to the properties of the traction fluid composition obtained. The following traction fluid compositions were obtained using the above described preparation method:

Traction fluid composition A comprising Traction Polyglocol A (30 wt percent) and Idemitsu Traction Fluid (70 wt percent), a traction fluid marketed by Idemitsu Kosan Co., Ltd, Japan, (Example 10);

Traction fluid composition B comprising Traction Polyglycol B (30 wt percent) and Hydrocal 1000, a traction fluid marketed by Calumet Lubricants Co. of Indianapolis, Indiana, U.S.A., (Example 11);

Traction Fluid Composition C comprising Traction Polyglycol C (30 wt percent) and Diala AX Oil (70 wt 5), a lubricating oil sold by Shell Corporation, (Example 12); and

Traction Fluid Composition D comprising Traction Polyglycol E (30 wt percent) and Diala AX Oil (70 wt percent), sold by Shell Corporation, (Example 13).

These traction fluid compositions remained as clear solutions or slightly hazy mixtures when they cooled to room temperature.

Traction coefficients of the polyglycols and traction fluid compositions of the present invention as well as commercial traction fluids were measured in a "mini-traction machine" marketed by PCS Instruments. The machine uses a ball-on-flat arrangement. The ball and disc are independently driven by motors, allowing the entrainment speed, *U* and slide-roll ratio, SRR to be independently controlled. The tests are carried out in fully-flooded conditions with the test fluid covering the upper disc surface. Temperature is determined by an embedded thermocouple in the pot wall and heat loss is minimized by a PTFE casing around the pot and cover. Temperature is controlled to plus/minus 1 °C. A piezoelectric force transducer was used to measure the latteral frictional force generated within the contact. Its precision was approximately plus/minus 0.005 N up to greater than 10 N. Traction tests were carried out using a 19 mm diameter steel ball on flat steel disc contact. Both balls and discs are hardened AISI 52100 steel and had rms roughness for the balls of 8 mm and the discs 15 mm. A new ball and disc were used for each liquid tested. For each fluid, traction curves were obtained from a single fluid sample in the sequence: (I) 30 °C, (1 GPa, 1.25 GPa); (ii) 60 °C, (1 GPa, 1.25 GPa); (iii) 90 °C (1 GPa, 1.25 GPa); and (iv) 120 °C (1 GPa, 1.25 GPa). The fluid tested and traction coefficients measured are shown in Table 1 below.

Table 1

Traction Fluid Composition	Test Temperature °C	SSR	Traction Coefficient @ 1 GPa	Traction Coefficient @ 1.25 Gpa
Composition A	30	2.5 percent	0.094	0.103
Composition A	60	2.5 percent	0.096	0.103
Composition A	90	2.5 percent	0.085	0.093
Composition A	120	2.5percent	0.066	0.079
Composition B	120	< 5 percent	0.0360	Not Determined
Composition C	120	< 5 percent	0.0282	Not Determined

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.